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Structural and optical properties of CdS nanoparticles

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Abstract : II-VI semiconductor nanoparticles have attracted a lot of attention due to the possibility of their applications in various devices. Among the materials used for fabrication of quantum dots (QD) and nanocrystals, cadmium sulphide (CdS) has drawn wide attention because of its potential for applications and availability of a variety of methods for its preparation. In the present study, chemical method has been used for synthesis of CdS nanoparticles in polyvinyl alcohol (PVA) as a matrix. X-Ray diffraction and electron microscopy (TEM) were used to determine the phase, shape and size of quantum dots. UV-VIS spectrophotometer and PL-study shows the blue shift and defect level formation within the band gap. Particle size was found to be between 4 and 7 nm.

Keyword : CdS quantum dot, bandgap, nanocrystallites.

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1. Introduction

Nanostructured materials, especially II-VI semiconductors have become a subject of intensive research for their extraordinary properties compared to their bulk counterpart [1–5]. The properties of semiconductor nanoparticles depend mainly on their shape and size due to high surface to volume ratio [6,7]. The structural and optical properties of CdS are of increasing interest due to the size dependent optical properties in the regime where the nanocrystal is smaller than bulk exciton radius. Blue shift of optical absorption spectrum, size dependent luminescence are some examples of the interesting properties exhibited by the nanoparticles [8–12]. All these properties are various manifestations of the so called quantum size effect which arises due to the increasing quantum confinement of the electrons and holes. However, when the dimensions of the crystallites become comparable to or less than the Bohr radius of exciton wave function, there is a significant change in properties. In CdS such quantum size effect is observed for crystallites below 5 nm diameter [13–15].

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Nanometer-scale electronics has opened new areas of application in device technology. One-dimensional nanoscale materials may be utilized in various nanodevices including nanologic circuits [16], nanolasers [17], nanosensors [18], nanothermometers [19], *etc.* Quantum dot of semiconductors and metallic alloys have been found to exhibit interesting optical properties. Several techniques such as thermal evaporation [20], sol gel process [21], metal-organic vapor phase epitaxy [22], wet chemistry deposition [23], spray pyrolysis [24], and chemical bath deposition (CBD) [25] have been used to produce CdS nanoparticles. Among them, chemical deposition is well known as a prevalent low-temperature technique for depositing large area of semiconductor nanoparticles, the simplest and the most economical one. A solution growth technique (SGT) is a relatively inexpensive and convenient technique for large area preparation of semiconductor nanoparticles at low temperature. The physical properties of the film are reproducible by this method. The growth process involves the application of a controllable chemical reaction which proceeds at a low rate in an aqueous solution containing the various reactants. The reaction rate in this technique is controlled by adjustment of *pH*, temperature, and the relative concentrations of the various reactants in the solution.

CdS nanoparticles are attractive candidate for opto-electronic applications, as the band gap of the semiconductors can be tuned to suit to any specific application. Bulk CdS has a hexagonal wurtize type crystal structure with lattice constant a = 0.4160 nm and c = 0.6756 nm. The single cubic phase has been observed in synthesised nanoparticles. In the present work, we report the chemical deposition of CdS nanoparticles and their characterization by XRD, TEM, SEM. UV-VIS spectro-photometry and PL spectrometry. The effect of pH on structural, morphological and optical properties of these films are investigated with the objective to optimize the conditions of the deposition process.

2. Experimental

CdS nanoparticles were synthesised using polyvinyl alcohol (PVA) as a matrix. PVA being a good solute to multiple phase systems capable of provoding uniform gap in the form of array. 5 wt% solution of PVA, $CdCl_2$ was added with various concentration (2, 3, 4 wt%) under a high stirring rate (200 rpm) condition using magnetic stirrer. The constant temperature 70°C for 3 hours was maintained. The sample under preparation was kept for 12 hours for complete dissolution to get a transparent solution. To this solution 2 wt% Na_2S was added till the whole solution turns into yellow colour. The CdS nanoparticle containing PVA were caste over precleaned glass slides to produce thin film form. The size of the particle is controlled by changing the *pH* value of the whole solution. The chemical reaction occurs as follows

$$CdCl_2 + Na_2S \rightarrow CdS + 2NaCl$$

pH controlled the rate of reaction due to the common ion effect. At higher *pH* the solubility product increases and as a result formation of CdS particle stops.

3. Results and discussion

3.1. XRD observation :

The XRD patterns of prepared sample were taken by Seifert XRD (3003 TT) operating at 40 KV–30 mA. The radiation source used was CuKα (λ = 1.542 Å) and a nickel filter was used to block K_β radiations. Figure 1 represent four different spectra of CdS nanoparticles with variation of *pH* with bulk sample (99.999% pure).

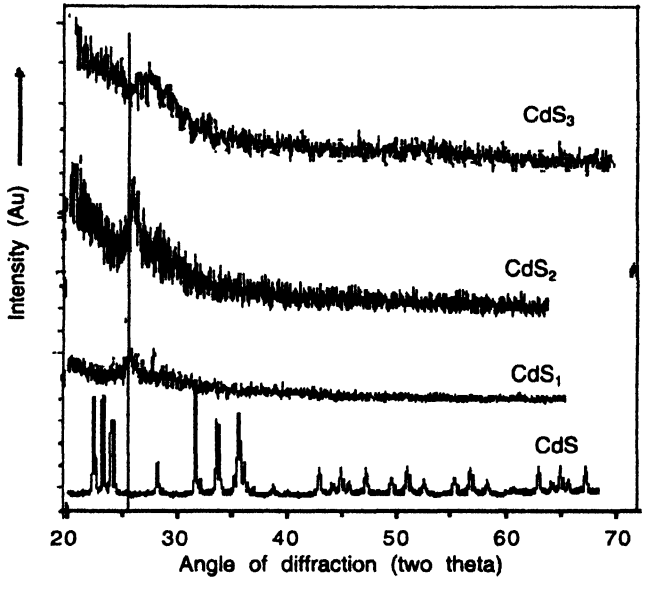

Figure 1. XRD traces of CdS for bulk, CdS_1 at *pH* 1.6, CdS_2 at *pH* 1.8 and CdS_3 at *pH* 2.0.

The XRD pattern of CdS_1 contain broad peaks at 2θ = 26.6 indicating the formation of nanostructure at *pH* = 1.6 and in CdS_2 shows broad peaks at 2θ = 26.8 and CdS_3 at 2θ = 27.1 respectively at *pH* = 1.8 and *pH* = 2

The XRD spectrum of both CdS_1, CdS_2 and CdS_3 apparently exhibit weak and broad peaks, suggesting small crystallite sizes of cubic phase (JCPDS 89-0440). Again it is seen that when the *pH* increases peaks are more broadened and shifted to higher diffraction angle with decreasing crystal size. The increase in diffraction angle is clearly a result of lattice contraction which is expected to occur because of higher surface to volume ratio [26]. Some separate peaks are also observed which may be due to CdO because XRD patterns were recorded in ambient condition. The change of phase from hexagonal wurtzite to cubic is observed in nanocrystallite as compared to their bulk counterpart. The grain size of the crystallite are estimated by Sherer formula [27]

$$D_{hkl} = K_\lambda / w \cos\theta \quad (1)$$

w being FWHM, θ is the Braggs angle and K = 0.89 for spherical shape (from TEM). For calculation w is observed by zooming the peak position using origin graphics

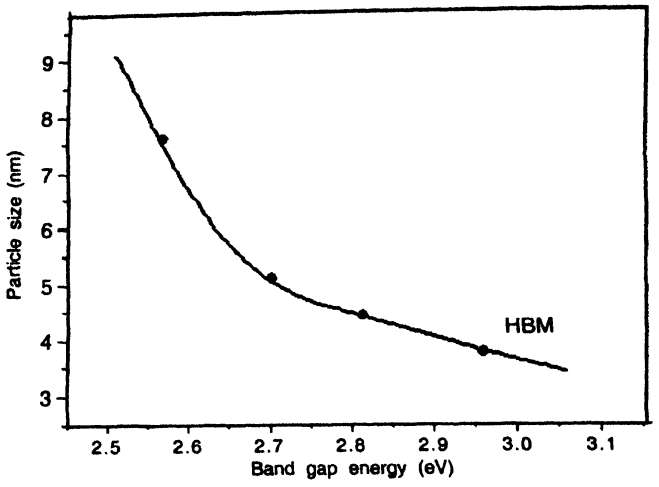

Figure 4. Band gap energy *vs.* particle size.

and at 610 nm for CdS_3. These spectra were recorded using (Thermospectronic AMINCO) luminance spectrometer. Emission bands redshifted from the absorption edge are observed in almost all of the semiconductor nanoparticles studied so far and are generally assigned to defect states. These redshifted emissions are usually associated with trapped states such as vacancies, interstitials, impurities, and surface defects [29]. It is seen that when the size of the nanocrystallite decreases the luminance is dominated by the band impurity. Also, surface passivation by sulpher has resulted in reduced emission intensity of this band indicating involvement of surface defects.

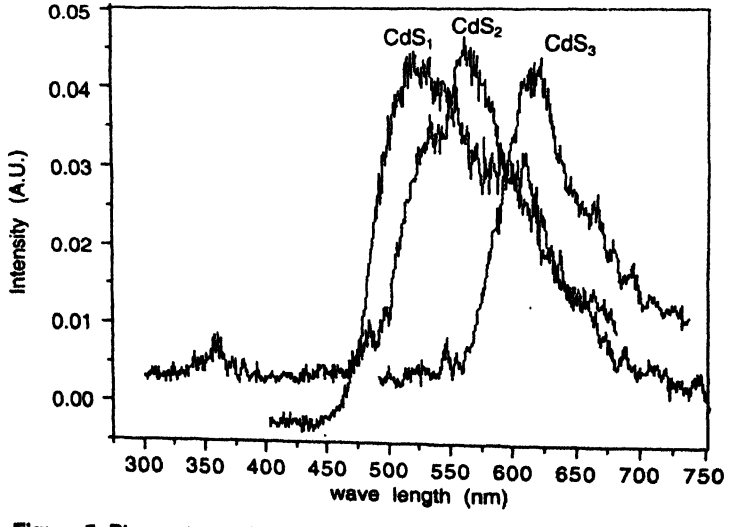

Figure 5. PL spectrum of CdS quantum dot at same excited wavelength 300 nm.

The nanostructure observed from TEM (model JEOL JEM-100cx) shows the

nanocrystallites to be spherical in shape. The size of the crystallite decreases with increase of *pH* which agrees with the result obtained from XRD observation.

The TEM photograph patterns Figures 6 and 7 were recorded using selected area observations and the particle sizes were determined in higher magnification (~2 × 10^5). The size of the particles obtained under various conditions are shown in Table 1. It is seen that optimum *pH* value for getting smaller nanoparticles is approximately 2. The PVA : $CdCl_2$ ratio also affects the size of the nanoparticles.

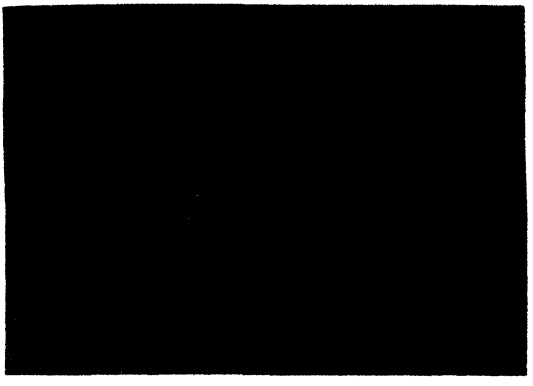

Figure 6. TEM image of CdS quantum dot at *pH* = 1.8

Figure 7. TEM photograph (zoomed view) of CdS quantum dot at *pH* = 2.

4. Conclusions

CdS nanoparticles of different crystallite sizes have been synthesized by the chemical route. The particle size is controlled by stirring rate, temperature of the solution, *pH* and time of stirring. The structural and optical characterization of the samples by XRD, TEM, UV-VIS spectrophotometer and PL show formation of CdS quantum dots having sizes between 4 and 7 nm. The optimum *pH* value for minimum size is found to be 2 and PVA : $CdCl_2$ ratio is found to 5 : 2 in our observations.

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